PATENT SPECIFICATION

NO DRAWINGS

867,783

Date of Application and filing Complete Specification: June 14, 1957.

No. 18850/57.

Application made in United States of America on June 14, 1956.

Complete Specification Published: May 10, 1961.

Index at acceptance:—Classes 2(6), P2C(8A: 8B: 13A: 14B: 20D1), P2D2A, P3A, P3C(6B: 8A: 8B: 12A: 13A: 13C: 14B: 20B: 20D1); 2(2), F(2F: 2G: 3A: 3E: 3F); 2(5), R1C(1: 6: 8: 9: 12: 15: 17), R3C(1: 6: 9: 17); and 95, A5.

International Classification:—C08d, f. C08b, g. C09d.

PATENTS ACT, 1949

SPECIFICATION NO. 867,783

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the seventeenth day of August, 1961, this Specification has been amended under Section 29 in the following manner:-

Page 1, *delete* lines 52 and 53 and *insert*:-

"There have been proposals hitherto to provide premixed pigmented beaded paints. One such proposal is in our Patent"

Page 1, line 55, *before* "paint" *insert* "marking"

Page 1, line 59, *after* "and" *delete* "to"

Attention is also directed to the following printer's errors:-

Page 2, line 115, *after* "which" *insert* "have"

Page 3, line 17, *for* "R" *read* "R"

Page 3, line 20, *for* "D" *read* "D"

Page 3, line 21, *for* "d" *read* "d"

Page 3, line 24, *for* "consideration" *read* "concentration"

Page 4, line 65, *for* "spigment" *read* "pigment"

Page 4, line 75, *before* "sub-" *insert* "angle"

Page 5, line 16, *before* "spray" *delete* hyphen

Page 6, line 1, *for* "alkyl" *read* "alkyd"

Page 6, line 5, *for* "alkyl" *read* "alkyd"

Page 6, line 22, *for* "alkyl" *read* "alkyd"

Page 6, lines 52/53, *before and after* "Registered Trade Mark" *delete* bracket

Page 8, line 27, *after* "coating" *insert* "composition"

THE PATENT OFFICE,
9th October, 1961.

DS 96808/1(5)/R.153 200 10/61 PL

PATENT SPECIFICATION

NO DRAWINGS

867,783

Date of Application and filing Complete Specification: June 14, 1957.

No. 18850/57.

Application made in United States of America on June 14, 1956.

Complete Specification Published: May 10, 1961.

Index at acceptance:—Classes 2(6), P2C(8A: 8B: 13A: 14B: 20D1), P2D2A, P3A, P3C(6B: 8A: 8B: 12A: 13A: 13C: 14B: 20B: 20D1); 2(2), F(2F: 2G: 3A: 3E: 3F); 2(5), R1C(1: 6: 8: 9: 12: 15: 17), R3C(1: 6: 9: 17); **and 95, A5.**

International Classification:—C08d, f. C08b, g. C09d.

COMPLETE SPECIFICATION

Improved Liquid Reflective Coating Compositions

We, MINNESOTA MINING AND MANUFACTURING COMPANY, of 900 Bush Avenue, Saint Paul 6, Minnesota, United States of America, a corporation organized under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to liquid reflective coating compositions containing admixed glass beads, which can be used to provide a reflective coating in one step in making highway signs and markers that have brilliant long-range visibility when viewed at night by motorists.

A well known way of making reflex-reflecting sign areas is to coat the base with reflective paint and, while it is still in a soft and tacky state, apply suitable glass beads to the surface so as to form a layer of beads partially embedded in the paint. Thus, for example, see the Specification of our Patent No. 556,935. This procedure requires two steps and requires care and skill to obtain an optically efficient, durable sign product. The paint coating must be applied in an accurate thickness relative to the size of the beads. If a quick-drying paint is employed, the viscosity and adhesion properties of the coating film rapidly change as it dries, so that the beads must be applied in just the right way to become securely bonded and properly positioned. If a slower-drying paint is employed, the beads may sink in too far during the drying period, and moreover there is delay in finishing the sign-making operation. In either case, the beads are applied against the surface of the wet or partially dried paint film. Its surface properties and viscosity which alter during drying, affect the nature of the bead-paint bond and the force of capillarity which determines the way in which the wet paint crawls up on the beads and the resultant physical structure. In order to provide unform durable sign surfaces it has been common practice to employ prefabricated reflex-reflecting beaded sheeting manufactured under controlled factory conditions, which the sign maker cuts and affixes to the sign base.

The only proposal to provide a premixed pigmented beaded paint has been in our Patent No. 641,547 wherein there is described a pigmented reflective highway paint containing transparent glass beads suspended in a paint. This paint did not reach its full effectiveness until it had been exposed for a time to the elements and to the reaction of traffic. In contrast thereto the present paint is ready to function as a reflex reflecting coating immediately upon drying.

The natural expectation would be that this result could not be obtained because in the applied paint coating the beads would be surrounded by the opaque reflective pigment, producing external surface reflection and scattering of light rays so that the beads and underlying pigment would have no opportunity to function in the manner required for obtaining reflex-reflection. So far as is known, this has been the view of the matter in the industry during many years, and the possibility of formulating compositions of the present type has only now been unexpectedly discovered.

In accordance with the invention there is provided a liquid coating composition which upon application to a substrate and after drying becomes immediately reflex-reflecting. The composition comprises a mixture of varnish solution, as hereinafter defined, finely divided metal flake reflective pigment and transparent microspheres of glass having a refractive index of at least 1.8, the pigment particles being of substantially smaller size than the microspheres, and the coating when applied to a substrate and dried providing a reflex-reflecting area having optically exposed

[*Price 3s. 6d.*]

Price 4s 6d.

Price 25p

microspheres associated with the reflective metal flake pigment particles contiguous to the back surface of the microspheres.

The liquid coating composition of the invention can be applied to desired base surfaces by brush, knife coat, screen process and spray methods, similarly to the application of conventional paints, to provide reflex-reflecting letters, symbols, designs, stripes or backgrounds, employed exclusively or in combination with reflective or non-reflective areas of other kinds, in fabricating complete signs and markers.

The reflex-reflecting characteristic of the dried coating on the sign or marker is due to the con-joint optical properties of the optically exposed surface layer of the transparent glass microspheres in combination with the finely divided metal flake reflective pigment particles associated with the back surfaces of the beads, this structure being held together and bonded to the underlying surface by the transparent varnish binder in which the beads and metal pigment are completely embedded. The microspheres serve as sphere-lenses and refract the light rays impinging on the reflective area, both before and after reflection from the underlying metal pigment particles, in such a way that a brilliant cone of light is reflected back toward the source of light. This is true even when the sign or marker is illuminated by a beam of light which strikes it at a substantial angle away from the perpendicular, as is commonly the case when a roadside sign or marker is illuminated at night by the headlight beam of a vehicle moving along the road. The result is that the sign or marker appears much brighter to the occupants of the vehicle than does a conventioneal sign or marker which lacks this reflex-reflecting characteristic. The sign or marker attracts greater attention and is readily visible at much greater distances.

Upon application to the base surface, the glass beads flow out to form a mono-layer containing tens of thousands of the glass beads per square centimeter. The varnish drains from the glass beads during evaporation of the solvent. The dried varnish film forms a thin transparent skin over the tops of the beads so that the outer surface has a corresponding spherulate or lenticular contour exposed to the atmosphere. The proportion of varnish binder solids is however sufficient to provide secure anchorage of the beads to the base surface. During the drying period and while the varnish solution is still fluid, a rather amazing motion of the metal flake pigment particles occurs. These flakes are smaller than the beads. The flakes which initially overlie the beads slide off the front hemispheral surfaces of the beads, thereby optically exposing the beads to incident light rays. Efficient reflection is provided by flakes which move into position to face toward the back hemispherical surfaces of the beads, in contact therewith or in close proximity, thereby providing each bead with a concentric reflector contiguous to its back surface. The flakes are secured in the necessary relationship to the beads by the time the varnish has become too viscous to permit their movement. The result is that incident light rays can pass through the beads to the back reflectors and be reflected back through the beads towards the source of light, so that the dried coating has an efficient reflex-reflecting characteristic. This effect is obtained regardless of whether the coating composition is applied to a vertical or to a horizontal surface or even to the underside of a horizontal base (such as a ceiling).

The present result is not obtainable with non-metallic pigments such as the non-shiny metal oxide pigments commonly employed in paints. Nor is it obtainable with any and all mixtures of beads, reflective metal flakes, and varnishes. A proper selection and proportioning is needed in accord with principles hereinafter indicated, in order that each ingredient function in harmony with the other ingredients to produce the desired result.

The optimum size of the glass beads to obtain good functional efficiency, coatability and dispersion and suspension in varnish vehicle, is in the range of about 25 to 75 microns (about 0.001 to 0.003 inch) diameter.

The beads must have a refractive index of at least 1.8. The optimum value is about 1.9 to obtain efficient reflex-reflection when the above-mentioned coating procedure results in a spherulate varnish surface exposed to the atmosphere for viewing under normal dry conditions. The optimum value is about 2.5 if the surface is covered with water under viewing conditions. A composition containing a mixture of beads of about 1.9 index and of about 2.5 index has advantages when used for coating outdoor surfaces exposed to wetting by water or rain (as in the case of marker buoys and bridge abutments) since the two types have optimum reflex-reflecting efficiencies when the spherulate surface contacts air or water respectively. Beads of such high refractive indices are to be distinguished from ordinary glass beads which a refractive index of about 1.5 and cannot be used for present purposes.

The metal flake pigment must provide efficient metallic (shiny) reflection. The particle size must be substantially less than the particle size of the beads. The flakes permit of pigment leafing. Aluminium powder leafing pigments, preferably extremely fine, are desirable because of relative low cost in relation to high efficiency, but other metal flake pigments can be used such as bronze powder, copper flake, tin flake, German silver flake, nickel flake, and even gold and silver leaf although too expensive for ordinary use. The optimum proportion is one that suffices to provide complete reflec-

tive areas at the backs of the beads without substantial excess of pigment serving no useful purpose, and this will vary depending upon factors such as the particular pigment and the size of the beads, but can readily be determined by trial in any given case. In general, it has been found that the optimum value lies in the range of one part by weight of pigment per 5 to 50 parts by weight of glass beads, although as little as one part pigment to 200 parts glass beads has given good results when an extremely fine aluminium leafing powder has been used. A useful formula for estimating the approximate maximum ratio for efficient reflection has been found to be:

$$R = 0.1(A)(D)(d)$$

where R is the weight ratio of glass beads to pigment, A is the surface area in square centimeters covered by 1 gram of leafed-out metal flake pigment, D is the density of the glass beads, and d is the mean diameter of the beads in centimeters.

Another factor to be considered is the "bead volume consideration" (BVC) by which is meant the percent. ratio of the volume of the glass beads to the total volume of glass beads, pigment and vehicle solids (varnish solids on dry basis). The volume of the beads means the actual volume of the beads themselves, and not the bulk volume of a mass. The volume per unit weight of each of the materials can readily be determined so as to facilitate making the BVC computation from weight data. The BVC value should be in the range of about 50 to 85%. Too low a value results in inadequate flow-off of binder and pigment from the bead tops. Too high a value results in a dried coating that is too weak or is punky or brittle. If the composition is to be applied to porous base surfaces that will absorb appreciable binder solids from the wet applied coating, thereby materially reducing the proportion of binder solids in the coating proper and unduly increasing the BVC value, allowance must be made for this in compounding the coating composition by including a correspondingly greater proportion of binder solids. In this situation it is preferable to employ a varnish having a gelatinous body so as to prevent or minimize absorption by porous base surfaces.

The composition can include volatile solvent to provide adequate fluidity when applied although this is not essential. The proportion of volatile solvent used, if any, depends upon the nature of the particular composition and the application procedure to be employed, and can best be determined by trial in any given case. A low viscosity resin for instance may not require any volatile solvent present. In general, varnish solutions formulated so as to contain non-volatile binder solids in the weight range of about 5 to 30% (and, correspondingly, 95 to 70% of volatile solvent material) have proved useful, as illustrated by the working examples hereinafter described.

The term "varnish" is employed throughout this specification in its broad sense and includes not only oil and spirit resin varnishes but lacquers as well, which provide adequately durable transparent film coatings when coated and dried. A liquid varnish vehicle is a mixture of non-volatile film-forming binder material (commonly referred to as the varnish solids) and of volatile solvent material which imparts the desired degree of fluidity and which evaporates during drying of the coating. Alkyd resin varnishes have been employed in obtaining reflective coatings according to the present invention that have prolonged resistance to outdoor exposure including resistance to darkening by the sun's rays. For temporary signs, nitrocellulose lacquer formulations have proved satisfactory. The varnish solution is thixotropic, having a "false body" which appears to assist the process of relocation of the metal flake pigment particles in the applied coating as previously described, and also serves to retard settling of the beads and pigment during storage of the composition. The inclusion of a small proportion (preferably less than one percent) of a colloidal suspending agent in the liquid coating composition is advantageous in producing a more stable and thixotropic suspension of beads and pigment, and in preventing clumping of pigment particles, thereby improving the shelf life. Illustrations of such additives are the organic derivatives of bentonite sold under the Registered Trade Mark "Bentone" by the Baroid Division of the National Lead Company. Even when prolonged storage has resulted in marked settling of beads and pigment, they can be redispersed before use of the composition by vigorous agitation or stirring, as by using a paint shaker or a propeller mixer.

When colourless glass beads and binder are used, the light reflected from the coating will have the colour of the reflective metal pigment. Thus silvery reflection is obtained when aluminium pigment is employed. In such case the day appearance will be dull, viewing being by diffused daylight; thus the sign area will have dull gray daytime appearance when aluminium pigment is used. This is not objectionable in many situations, but attractive colour effects both by day and night can readily be obtained by compounding the coating composition so as to include material that will have a colour filter effect without impairing the transparency of the elements of the coating that must transmit light rays. Thus coloured glass beads can be utilized, made from transparent coloured glass or provided with transparent coloured coatings. Transparent pigment (such as phthalocyanine pig-

ment) can be included so as to colour the binder, this pigment having approximately the same refractive index as the binder so as not materially to interfere with transparency, or a dye can be employed.

The dried coating of the present type provides a reflective area upon the base surface having a vast number of reflex-reflecting spots per square inch or square centimeter, each consisting of a minute glass bead having a metal flake reflector concavely shaped to be contiguous to the back surface, forming a reflex-reflecting catadioptric combination. The human eye cannot distinguish between the light rays emanating from adjacent individual spots, and so the reflective area appears to the viewer of the sign or marker as a uniform continuous area. The viewer's reaction under reflex-reflecting viewing conditions is that the area is coated with an extraordinarily brilliant paint. This is true even when the incidence of the illuminating light beam is at a substantial angle away from the perpendicular, when the sign is viewed by people located near the axis of the incident light, and hence the signs have what is known as good reflex-reflection "angularity," also known as "wide-angle" reflex-reflection. This means that highway signs and markers have good night-time visibility to motorists even when they do not face substantially directly toward the observer, and even when they have a curved surface (as in the case of posters tacked on telephone poles and in the case of painted tree trunks).

In contrast, a mirror type of sign or marker provides specular reflection and returns reflected rays toward the source only when an angle of incidence is zero (i.e. when the rays impinge perpendicularly to the surface of the mirror). A surface coated with a conventional aluminium paint (dried varnish containing leafed-out aluminium flakes) provides semi-specular reflection, and visibility is poor for persons located near the axis of an angularly incident beam of light. Signs and markers of these types must be viewed from approximately dead ahead to have good visibility. This prevents general utility for roadside signs and markers, since they are ordinarily so located that they can be viewed from dead ahead (if at all) for only an instant from a rapidly moving vehicle.

An ordinary painted or enamelled sign surface provides non-specular or diffused reflection, owing to the reflection characteristic of the jagged pigment particles which causes a beam of light to be reflected in all directions. Some light rays are reflected in the direction of the source of an angularly incident beam of light, but most of the light is scattered in other directions. A glossy enamelled surface exhibits specular surface reflection in addition to the diffused reflection provided by the spigment particles, which further reduces visibility to persons located near the axis of an angularly incident beam of light.

The following table illustrates the relative reflection intensities for various samples as measured by a photometer located close to the beam of incident light, the divergence angle being one third of a degree and being representative of the average divergence angle encountered in typical highway viewing conditions. (The divergence angle is the subtended between straight lines connecting the light source to the reflective area and connecting the reflective area to the viewing eye or photometer). The reflection intensities are shown for angles of incidence of 10°, 20°, 30° and 40°. (The angle of incidence is the angle subtended between a straight line connecting the source to the reflective area and a line perpendicular to the plane of the reflective area). The same light beam source was used for all measurements. In each instance the value given is the ratio of the photometer reading for the sample being tested to the reading for a typical glossy white enamelled sign surface (used as a comparison standard), both having the same area and being measured at the same angle of incidence.

Reflective surface	Relative reflection intensities at designated angles of incidence			
	10°	20°	30°	40°
White sign enamel (diffused reflection)	1	1	1	1
Aluminium paint (semi-specular reflection)	0	0	0	0
This invention (reflex-reflection)	125	125	115	100

In this table the "zero" values for the aluminium paint sample signify values which are very small compared to those for the white enamel sample. The former type has a dark grey appearance when visual comparison is made at the designated angles, and has a

brilliant silvery appearance only when viewed from substantially dead ahead.

The above noted sample prepared with the reflective coating composition of this invention was made by screen process coating a white showcard stock with the composition of Example A (given hereafter) using glass beads of 1.9 refractive index having diameters in the range of 20 to 45 microns. These are representative of values obtainable with a variety of compositions, and even higher values have been obtained with some of the present compositions.

The invention makes possible highly effective reflective coating compositions than can be utilized in aerosol "bomb" or "-spray-can" applicators from which the composition can be sprayed on any surface. The pressure is provided by a volatile propellant liquid having a high vapour pressure that is included in the vessel. For example, the reflective coating composition can be readily sprayed on bridge abutments, concrete curbings, posts and tree trunks to provide brilliant visibility at night to motorists and serves as a guide or as a warning of a hazard. The daytime appearance is not materially changed owing to the inconspicuousness of the coating except when viewed under reflex-reflecting conditions. A highway patrolman can carry a small applicator in his car or motorcycle and can conveniently stop and coat any object that appears in need of greater nighttime visibility. The compositions can also be sprayed from a spray-gun.

Temporary highway safety markers and signs can be easily prepared. There is also a market for temporary advertising signs that are inexpensive and have high visibility at night to motorists. Examples are signs advertising special sales and posters used during political campaigns. These can readily be made in quantity, as by spraying the reflective coating composition on inexpensive cardboard backings (such as showcard stock) using a stencil procedure, or by screen process printing.

The invention also permits the production of a reflex-reflecting coating that has a smooth flat outer surface as contrasted with the spherulate or lenticular exposed surface that results when only the previously described one-step procedure has been employed. This can be accomplished by a composite structure formed by first providing a coating of the beaded reflective composition and allowing it to dry, and then coating the spherulate surface with a transparent varnish, coloured or clear, which covers the protrusions and provides, when dry, a flat outer surface. In this situation, the theoretical optimum refractive index of the composite is about 2.8 but a lower value can be used with good results. As is known in the art, by providing a glass bead with a concentric transparent coating having a lower refractive index than the glass of the bead the refractive index of the coated bead will be higher than the uncoated bead, so that the focal relationship of the bead and back reflector in the final coating structure is altered to produce a reflection characteristic similar to that obtainable with a uniform sphere lens of higher refractive index, thus avoiding the need of glass of very high refractive index.

The following examples provide illustrations of presently preferred varieties of reflective coating compositions of this invention.

EXAMPLE A

The following formulation is well-adapted for application by screen process and knife coating procedures on various paper and metal base surfaces in making signs and markers.

	% by weight
Beads of glass having a refractive index of 1.9 (diameter range of 20 to 45 microns)	59.00
Nitrocellulose mixture (5000 second viscosity type wet with 35% ethanol)	1.90
Oil-modified alkyd varnish resin solution (50% solution of alkyd resin in xylol)	6.45
Dibutyl phthalate (plasticizer)	0.23
Aluminium pigment paste (fine lining aluminium flake milled with 60% butyl lactate)	5.87
Butyl lactate	13.85
Xylol	11.30
Butanol	1.40

A preferred type of alkyl resin solution for this purpose is available under the Registered Trade Mark "Beckosol 1307" and is a solution of medium oil length, soya-modified, phthalic alkyl resin (drying type) in 50% of xylol solvent.

A preferred type of aluminium pigment is an extremely fine aluminium leafing powder, also known as fine lining aluminium flake, of which 1 gram covers a surface area of 25,000 square centimeters. The paste is prepared by ball milling the aluminium pigment with the butyl lactate for 16 hours or longer.

The composition is prepared by charging the butanol and xylol solvents to a mixing vessel. The nitrocellulose (wet with ethanol) is added and the mixture is stirred until the nitrocellulose is thoroughly wetted and pulped. The butyl lactate solvent is slowly added with stirring which is continued until a clear solution is obtained, after which the dibutyl phthalate and the alkyl resin solution are added with continued stirring. The aluminium pigment paste and the glass beads are sucessively added with thorough mixing to obtain a good dispersion. The product is then ready for packaging.

The weight and volume percentages on a dry solids basis (disregarding all volatile components) are the same as in a dried coating and are as follows:

	% weight	% volume
Glass beads	89.3	77.8
Aluminium pigment	3.6	4.2
Varnish solids	7.1	18.0

Thus it is evident that the bead volume concentration (BVC) as previously defined, is approximately 78% and that the total volume concentration of beads and pigment is 82%. The weight ratio of glass beads to pigment is 25:1. In the liquid coating composition the varnish vehicle (exclusive of beads and pigment) is comprised of 13.3% non-volatile plasticized binder solids (nitrocellulose, oil-modified alkyd resin and dibutyl phthalate) and 86.7% volatiles (ethanol, butanol, xylol and butyl lactate) by weight.

EXAMPLE B

The following abbreviated formulation is similar to that of Example A except that an organic derivative of bentonite is included to improve thixotropic and suspension properties, producing a more stable product. A preferred example of such compound is available under the "Bentone 18-c" (Registered Trade Mark) from the Baroid Division of the National Lead Company, and is believed to be identifiable as an alkyl ammonium montmorillonite.

	% by weight
Glass beads as in Example A	55.00
Nitrocellulose mixture	1.90
Oil-modified alkyd resin solution	6.70
Dibutyl phthalate	0.23
Aluminium pigment paste	4.55
Bentonite derivative paste (75% ethyleneglycol monoethylether)	2.00
Butyl lactate	16.35
Xylol	11.80
Butanol	1.47

The bentonite derivative paste is prepared by mixing the bentonite derivative and the ethyleneglycol monoethylether in 25:75 ratio and then working twice through a three-roll paint mill to form a fairly stiff lump-free paste.

The composition is compounded as described in Example A except that just prior to admixing the glass beads, the bentonite derivative paste is stirred in and the bath is heated to 120° to 130°F. with continued stirring until smooth and free from lumps.

EXAMPLE C

The following formulation employs an air-drying alkyd resin varnish base as distinguished from the nitrocellulose lacquer type varnishes of Examples A and B. It provides an excellent suspension of the glass beads and it can be brushed or sprayed on many types of surfaces, including metal, wood, paper, and concrete, to provide dried coatings having excellent reflex-reflection properties. This composition lends itself to use in aerosol spray containers, which can be loaded with this composition and an equal amount of fluorinated propellant (such as a mixture of equal parts of "Freon 11" Registered Trade Mark and "Freon 12" Registered Trade Mark) together with a steel ball so that shaking of the container will ensure a good dispersion at time of use.

	% by weight
Glass beads as in Example A	62.75
Polyamide modified alkyd resin (gelled with 60% mineral spirits)	19.56
Fine lining aluminium flake	1.97
Naphtha (V.M. & P.)	12.90
Mineral spirits (thinner)	2.54
Metal naphthenate drier (50% solution)	0.23
Anti skinning agent	0.05

The anti-skinning agent was that obtained under the trade-name "Exkin # 1" from Nuodex Products Company which is a division of Heyden Newport Chemical Corporation of Elizabeth, New Jersey. This product is believed to be a butyraldoxine.

A preferred polyamide modified alkyd resin, which is desirable because of its thixotropic properties is available under the trade name "Burnok" from the T.F. Washburn Company, Chicago, Illinois. Metal naphthenate varnish driers are well known to the art (e.g., a mixture of cobalt, manganese and lead naphthenates). Anti-skinning agents are also well known in the varnish art and prevent or minimize the formation of a surface spin upon exposure to the atmosphere.

The composition is prepared by charging the alkyd resin gel to a mixing kettle and vigorously agitating. The naphtha and mineral spirits are slowly added with mixing and heating to 100°F. to obtain a smooth mixture. Then the aluminium flake pigment, metal naphthenate drier and anti-skinning agents are added and worked in. As the batch cools and becomes more viscous the glass beads are stirred in and dispersed.

EXAMPLE D

The following formulation illustrates the use of a synthetic rubber type base. It is useful in screen process printing on cloth to provide reflex-reflecting designs thereon that are highly flexible, as on warning flags, tarpaulins and clothing it can also be employed on rubber, leather and plastic articles.

	% by weight
Glass beads as in Example A	39.0
Phenolic varnish resin (heat-advancing oil-reactive 100% phenol-aldehyde resin)	4.6
Coumarone resin	1.5
Neoprene rubber mix (100 parts polychloroprene rubber milled with 5 parts ZnO, 4 parts calcined MgO, 1.5 parts sodium acetate and 2 parts of the antioxidant of the antioxidant obtained under the trade name "Neogone A")	6.2
Aluminium pigment paste (milled with 60% butyl lactate)	4.7
Ethanol	0.5
Toluene	29.0
Butyl lactate	14.5

The ethanol and half of the toluene are charged to a mixing vessel. The phenolic resin and the cumarone resin (such as Cumar W Registered Trade Mark) are mixed in, and then the neoprene rubber mix is added with continued stirring until a smooth mixture is obtained. The remaining toluene and the butyl lactate are added, following which the aluminium pigment paste and the glass beads are incorporated.

WHAT WE CLAIM IS:—

1. A liquid coating composition which upon application to a substrate and drying becomes immediately reflex-reflecting, comprising a mixture of varnish solution, finely divided metal reflective pigment, and transparent microspheres of glass having a refractive index of at least 1.8 the pigment particles being of substantially smaller size than the microspheres, and the coating when applied to a substrate and dried providing a reflex-reflecting area having optically exposed microspheres associated with the reflective metal flake pigment particles contiguous to the back surfaces of the microspheres.

2. A coating according to Claim 1 wherein the microspheres have a diameter of 25 to 75 microns.

3. A coating composition according to Claim 1 or Claim 2 wherein the microspheres are present in a bead volume concentration of 50 to 85%.

4. A coating composition according to any preceding claim wherein the metal flake pigment is aluminium.

5. A liquid coating composition as described herein.

For the Applicants:
LLOYD, WISE, BOULY & HAIG,
Chartered Patent Agents,
10, New Court,
Lincoln's Inn,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.